

is met with in the central portion of thick bars of Swedish iron, kept for some weeks at a temperature below their melting point, but high enough to give rise to recrystallisation. We then get a complete separation of free iron from a compound containing some carbon, and a crystalline structure which, as far as mere form is concerned, most closely corresponds with that of meteoric iron, as may be at once seen on comparing them.

These facts clearly indicate that the Widmanstätt's figuring is the result of such a complete separation of the constituents and perfect crystallisation as can occur only when the process takes place slowly and gradually. They appear to me to show that meteoric iron was kept for a long time at a heat just below the point of fusion, and that we should be by no means justified in concluding that it was not previously melted. Similar principles are applicable in the case of the iron masses found in Disco, and it by no means follows that they are meteoric because they show the Widmanstätt's figuring. Difference in the rate of cooling would serve very well to explain the difference in the structure of some meteoric iron, which do not differ in chemical composition; but, as far as the general structure is concerned, I think that we are quite at liberty to conclude that all may have been melted, if this will better explain other phenomena. On this supposition we may account for the separation of the iron from the stony meteorites, since under conditions which brought into play only a moderate gravitative force, the melted iron would subside through the melted stone, as happens in our furnaces; whilst at the same time, as shown in my paper read at the meeting of the British Association in 1864, where the separating force of gravitation was small, they might remain mixed together, as in the Pallas iron, and others of that type.

In conclusion I would say that though from want of adequate material for investigation I feel that what I have so far done is very incomplete, yet I think that the facts I have described will, at all events, serve to prove that the method of study employed cannot fail to yield most valuable results, and to throw much light on many problems of great interest and importance in several different branches of science.

MENDELEEF'S RESEARCHES ON MARIOTTE'S LAW¹

FROM researches on the depression of the mercury results the possibility of introducing a precise correction relative to the volume of gas contained between the surface of the mercury and the horizontal plane which touches the summit of the meniscus. In all my researches I introduce each time a correction relative to this volume.

The volume of the reservoir which contains the mercury and the gas under various pressures undergoes two kinds of variations; first, those which are due to the difference between the pressures which act on the two sides of the vessel, and second, those which depend on differences in the volume of mercury. The compressibility of the reservoirs employed in the researches has been always determined by experiment, and their change of volume produced by the introduction of mercury can be determined by surrounding the vessel filled with mercury by another filled with the same material. When the height in the two vessels is the same, the capacity of the vessel is that which exists at the time of equality of pressure on the external and internal surfaces of the vessel. If we empty a part of the external vessel the capacity of the vessel changes in the same manner as when we fill or when we empty the vessel. Experiments of this kind have shown the possibility of determining the changes of capacity depending on the quantity of mercury. The relative corrections have in each case been introduced into the calculations.

All the practical side of the subject—the desiccation of the gas, the complete abstraction of the remains of the gas from the apparatus, the hermetical junction of the parts of the apparatus by means of mastic and mercury stop-valves, the means of main-

taining the gases and the mercury at a constant temperature, the calibration of the tubes, and a number of other details have had to be elaborated more or less anew. All this will be found described in my work "On the Elasticity of Gases." I have published this work only in Russian, not having means sufficient to publish a translation of a work so voluminous, and desiring to conform to the custom existing among *savants* of all countries of describing their labours in their mother-tongue, in order to present to the scientific literature of the country where they live and work a gift in proportion to their powers.

My desire was to investigate the subject in its minutest details in order to eliminate every possibility of doubt as to the causes which determine the deviations observed from the Boyle-Mariotte Law. I know that that law is firmly established, and I believe it will remain so. Not less great is the certainty in the mind that rarefied gases approach the perfect state. That certainty I had also on commencing my experiments. It was necessary then to determine as completely as possible all the circumstances on which depend the facts contrary to the opinion generally held. This is why I have modified the apparatus, improved the methods, and employed in this work more than three years without interruption. Now so far as regards low pressures the work is finished, and I have obtained definitely certain proofs of the rigorous accuracy of my first observations.

The experiments which I have made with Kirpichoff have proved that not only for air, but also for hydrogen, and even for carbonic acid, the deviations are positive when the gas is subjected to a very small pressure; it is found, moreover, that these deviations increase in proportion to the variation from the normal pressure. The same thing has been found in a new series of experiments undertaken by me with M. Hemilian. The experiments are described in tome ii. of my work on the "Elasticity of Gases," which I have just published. A brief extract on this subject is published in the *Ann. de Chimie et de Physique*, October, 1876. I shall quote only the results obtained by us from the experiments made in 1875 and in the beginning of 1876.

Into a new apparatus we have introduced several further improvements, of which the chief are:—(1) The barometer, the metre, and the reservoir, containing the gas and the mercury, have been placed in the same bath full of water; (2) We have succeeded in producing a complete vacuum in the barometric chamber; (3) The bath was maintained at an almost uniform temperature by means of an agitator, and the small differences in the temperatures of the various layers have been determined by a differential thermometer; (4) The junction between the air reservoir and the barometer has been made, not only without the aid of a tap, but also without the use of mastic.¹ Thus the gas was surrounded only by the glass and the mercury. We shall confine ourselves to a summary of the results of our experiments, made between 650 and 20 millimetres' pressure, with four gases—H, air, CO₂, and SO₂.

1. If, starting with a certain small pressure, we arrive at pressures smaller still, we find for all gases positive deviations, viz., $\frac{d(pv)}{dp} > 0$; the gases, then, are in this case less compressed

than Mariotte's Law requires. Similar deviations were also observed for hydrogen by M. Regnault between 1 and 30 atmospheres, and M. Natterer for all gases between 100 and 3,000 atmospheres.

2. Under small pressures and for all gases, the value of the positive deviations, i.e., the numerical quantity (or magnitude) $\frac{d(pv)}{dp}$, increases when the initial pressure diminishes. Thus,

for example, for hydrogen at 400 millimetres—

$$\frac{d(pv)}{dp} = +0.000002,$$

and at 120 millimetres—

$$\frac{d(pv)}{dp} = +0.000010.$$

3. For gases like CO₂ and SO₂ we find near the atmospheric pressure, negative deviations; e.g., for CO₂, $p_0 = 635$, $p_1 = 200$, $p_0 v_0 = 10,000$, $p_1 v_1 = 10,029$; but, under less pressures still, the deviations become positive even for CO₂ and SO₂. For example, for CO₂, $p_0 = 190$, $p_1 = 64$, $p_2 = 22$, $p_0 v_0 = 10,000$, $p_1 v_1 = 9,996$, $p_2 v_2 = 9,983$; for SO₂, $p_0 = 190$, $p_1 = 60$, $p_2 = 22$, $p_0 v_0 = 10,000$, $p_1 v_1 = 10,010$, $p_2 v_2 = 9,996$.

4. The existence of positive and negative deviations for the

¹ To attain this end the gas-vessel and the branch of the barometer are soldered together by a capillary tube made of a single piece.

² Continued from p. 457.

same gas, observed by means of the same apparatus, according to the amount of pressure, and the conformity in the various series of experiments, prove that the results obtained do not depend on any constant errors in the methods employed, but that they are really caused by the nature and the essential qualities of the gases investigated.

5. The variations from Mariotte's Law under very weak pressures being very small, it is necessary, in determining them, to make the reading of the pressures, the volumes, and the temperatures (absolute $t = 273^\circ$) with a precision of two-thousandths of these total values; thus, e.g., if $p_0 = 0.200$ m., $p_1 = 0.100$ m., and $v_0 = 2,500$ gr., $v_1 = 5,000$ gr. of mercury ($t = 20$), it will be necessary to determine the pressures with a precision of 0.01 mm., the volumes to 0.1 gr. of mercury, and the temperatures to 0.1 of a degree.

The results will be doubtful if the precision is less.¹ Thus it is found that under a certain small pressure gases present positive deviations from Mariotte's Law; even gases like sulphurous acid and carbonic acid, which under high pressures show considerable negative deviations. It is the same with air. M. Regnault commenced his researches with pressures which exceeded that of the atmosphere, and obtained negative deviations.

In 1874 I effected with all the care possible the determination of the deviations for air under pressures of from 650 to 2,000 millimetres, and towards the end of 1875 and in the beginning of 1876, in a special apparatus provided with compound manometers, I repeated the same experiments with M. Bogusski for pressures from 700 to 3,000 millimetres with air, hydrogen, and carbonic acid. These researches proved the rigorous accuracy of M. Regnault's conclusions. Air and carbonic acid were found to be subject under these pressures to negative deviations, greater for carbonic acid than for air; and hydrogen, for these same pressures, was found to present positive deviations. At present we are continuing the same kind of experiments for pressures of more than three metres.

Thus hydrogen, under all pressures, commencing with zero and ending with a pressure infinitely great, presents throughout positive deviations; at no pressure does it follow Boyle's Law rigorously, and it never presents negative deviations. Increased pressures always give a greater volume than what might be expected according to the variation of the pressures. Air under pressures less than 600 millimetres also presents positive deviations; but under pressures greater than that of the atmosphere its deviations become negative, and under pressures which exceed 100 atmospheres its compressibility again becomes positive. Consequently for this gas there are two pressures at which it follows Boyle's Law; the one is very nearly that of the atmosphere, the other lies between 30 and 100 atmospheres. These pressures, under which the changes of the sign of compressibility occur, will be different for carbonic acid; viz., under pressures less than that of the atmosphere the change of sign is found at nearly 200 millimetres, and for higher pressures it commences near that which corresponds to 70 metres of mercury, if we base our researches on this point on the observations of Dr. Andrews on the compressibility of carbonic acid gas for temperatures above 31° . For lower temperatures this point will probably correspond to the passage of carbonic acid into the liquid state. Consequently with a change of temperature the pressure at which the change of sign of compressibility occurs, changes also. For sulphurous acid the sign of compressibility under pressures lower than that of the atmosphere changes at about forty millimetres of pressure. But even this gas, so easily liquefiable, under low pressures, has always a positive compressibility. There is not then, and there cannot be, a gas which is rigorously subject to Mariotte's Law under small pressures.

The idea of an absolute gas belongs, then, to the number of fictions which find no confirmation in facts. We cannot, then, suppose that with the decrease of density or with the increase of the *vis viva* of gaseous molecules, gases approach a state in which they follow Boyle's Law. Then (the density diminishing, the velocity of the molecules increasing, that is to say, the pressure diminishing, the temperature increasing, and the molecular weight diminishing) they all tend towards another state characterised by the expression $\frac{d(pv)}{dp} > 0$; i.e., they are assimilated to solid and liquid bodies, when the condensation reaches its limit. We

must believe that there is a limit of condensation and a limit of rarefaction. If we take, in fact, a mass of non-volatile liquid, and if we submit it to pressures infinitely great and infinitely small, we shall see it change volume; but in the two cases, we shall have finite volumes, capable of measurement, and even differing little for one and the same body. It is the same with gases, if we admit that for pressures approaching zero, gases contract according to the same law as that which we can deduce from our compression experiments under pressures less than that of the atmosphere, or as hydrogen contracts. Under great pressures, or under pressures excessively small, every gas resembles a solid or liquid body, and possesses two limits of compressibility. The volumes which correspond to these limits are very different, but there is always reason for believing that they exist.

Without launching into hypotheses to explain these limit volumes (such, e.g., as the supposition that molecules in themselves possess volume), I will confine myself to the question of the matter of celestial space. What is the luminous ether? One of two things—either an elastic independent matter, *sui generis*, or the gas of the atmospheres of celestial bodies, considerably rarefied. In the latter case it is necessary to admit the absence of limits in the atmospheres and a condensation of the ether greater and greater in proportion as we approach a celestial body (sun or planet). There are many arguments for and against both hypotheses. On the one hand, spectrum analysis leads us to conclude that the material of all heavenly bodies is identical; on the other hand, it proves the diversity of the composition of atmospheres. This is why we abstain from solving the question in its essence. But spectrum analysis does not speak less in favour of the former hypothesis, because it shows the diversity of composition of our terrestrial atmosphere from that of many of the other celestial bodies. In the researches on the resistance of celestial matter to the movement of the planets, there appears also to be a confirmation of the former of these two hypotheses, for neither planets nor comets show any diminution in the excentricity of their orbits, which would be an inevitable consequence of motion in a rarefied medium, as has been observed in the case of Encke's comet. Exact investigations on the movement of that comet, repeated in recent times by M. von Asten, the Pulkowa astronomer, show clearly the advances towards the sun at perihelion, although in the beginning M. von Asten had not noticed them. But that comet at perihelion was found only at one-third of the distance which separates the sun from the earth, i.e., it was nearer to the sun than Mercury. It is possible that it passed near to the limits of the solar atmosphere. Faye's comet, as is known, does not present these same diversities, but its perihelic distance is about 1.68 , that of Encke's comet being only about 0.33 ; it exceeds it then so much that their comparison would only serve to confirm the hypothesis of a solar atmosphere. If we admit a limit for the atmospheres, we must expect in gases, for small pressures, exactly that kind of variation from Boyle's Law which I observed in rarefied gases.

To prove that gases under very small pressures, as well as under very considerable pressures, vary from the Boyle-Mariotte Law by no means the same as to deny the truth of that law; I feel that I ought to state this most explicitly. For a long time the law of gravitation could not be made to accord with the perturbations; latterly these perturbations have proved the best confirmation of the laws of gravitation. In the present case it may be the same. There are three laws for gases: that of Boyle and Mariotte, $p v = \text{const.}$; that of Gay Lussac, $v t = v_0 (1 + \alpha t)$; and that of Ampère and Gerland $\frac{\alpha v}{m} = \text{const.}$ (α being the molecular weight, and m the mass). Their ensemble is expressed for all gases in general by the equation—

$$\alpha p v = 845 (273 + t) m,$$

where α is the atomic weight ($H = 1$), p the pressure in kilograms per square metre, v the volume in cubic metres, m the weight in kilograms, t the centigrade temperature. This is, however, only a first approximation. In the second member of the equation there must be additional terms which express a function of p and of α , very small for the ordinary mean values of p , and which become of a sensible magnitude only when p is very small or very great. To find this function is a question of the future, and demands the labours of a great number of investigators. My aim is to be able to furnish some experimental data which will permit of judging of the form of that function. This work requires many new processes, measuring apparatus of a high

¹ It is by these causes that the want of conformity in the experiments of Siljeström is sufficiently explained (*Pogg. Ann.*, April and May, 1874; see also the *Bull. de l'Acad. de Sc. de St. Pétersbourg*, t. xix, p. 466, and *Berichte der deutschen chem. Gesell.*, t. viii, p. 1,339; t. viii, pp. 576 and 749), and of M. Amagat (*Comptes Rendus*, April 17, 1876.)

